

UDC 532.783(045)

H. B. Bordyuh

MECHANISM OF DIMERIZATION OF VIOLOGENS IN LIQUID CRYSTALLINE MEDIUM

Institute of Information and Diagnostic Systems, National Aviation University, Kyiv, Ukraine

E-mail: a.bordyuh@gmail.com

Abstract—This work presents the analysis of experimental data on optical properties of viologens introduced to the liquid crystalline medium stipulated by the application of increasing voltage values. These data along with quantum mechanical theory allowed to specify the mechanism of dimerization of violoden molecules which leads to the colour change of the liquid crystal-viologen sample. Specifically, the dimerization of viologen molecules in liquid crystalline medium occurs due to interaction between viologen molecules, which were fully reduced under the action a voltage applied, and initial viologen molecules.

Index Terms—Lyotropic liquid crystals; viologens; optical spectroscopy; absorption; quantum mechanics.

I. INTRODUCTION

It was shown that combining lyotropic liquid crystals (LLC) with electrochromic impurities, namely viologens, allows for creating new class of liquid crystalline materials with regulated optical properties. Physical and chemical properties of such materials were widely investigated in series of works [1]–[3]. Possible practical applications require further investigations concerning intermolecular processes taking place under the action of an electric field and causing colour modifications of interest.

II. ANALYSIS OF INVESTIGATIONS AND PUBLICATIONS

It is known that application of an electric field leads to the reduction of viologen molecules and formation of coloured radical cations and dimers [4], [5]. Spectrometry data for LLC-viologen composites [6] showed that viologens reduce under the action of an electric field in the lyotropic liquid crystalline matrix with formation of blue-coloured radical cations and red-coloured dimers. Their formation is confirmed by the presence of characteristic absorption bands ($\lambda = 395, 605$ nm, and $\lambda = 365, 520$ nm, respectively) in spectra [6]. Dimerization could be stipulated by two different processes. According to the work [7] dimerization of viologens in water is caused by interaction between two radical cations when their concentration in a sample reaches some critical parameter. In recent works dimerization is associated with interaction between initial viologen molecules and molecules undergone two-electron reduction [8].

Thus, the **aim of the present work** was to combine all the known experimental data concerning formation of viologen dimers in liquid crystalline medium and to specify the mechanism of dimerization.

III. EXPERIMENTAL DATA

Voltamperometry and spectrometry experimental data indicate that in water-containing lyotropic liquid crystalline medium dimerization more likely passes in accordance with the second process. According to the volt-ampere characteristic [6] viologen molecules reduce in LLC matrix in two stages. The first stage (Curve 2, $U = 2,5$ V) corresponds to the formation of radical-cations, and the second one (Curve 3, $U = 3$ V) corresponds to the formation of colourless biradicals with plain quinoid structure. The last fact is confirmed by absorption spectrum (Fig. 1) which shows no significant absorbance at voltage value of 3 V. The dimerization process starts after increasing the voltage up to 4 V (Curve 4). Thus, dimerization cannot be caused by radical cation – radical cation interaction since there are no radical cations in the sample at voltage values exceeding 3 V as shown by absorption spectra (Fig. 1). However, initial or non-reduced viologen molecules could still be present in the volume of a sample moving towards electrodes under the action of an increased voltage and interacting with fully reduced molecules to form dimers.

IV. THEORETICAL JUSTIFICATION

For theoretical proof for the dimerization mechanism it is reasonable to turn to the quantum mechanics [9].

In the case of viologen dimerization we talk about the formation of so called physical dimers. Physical dimers form in the case of two equal molecules, which are located closer one to another than to other similar molecules and have specific orientation. At the same time they do not form any chemical bond with each other.

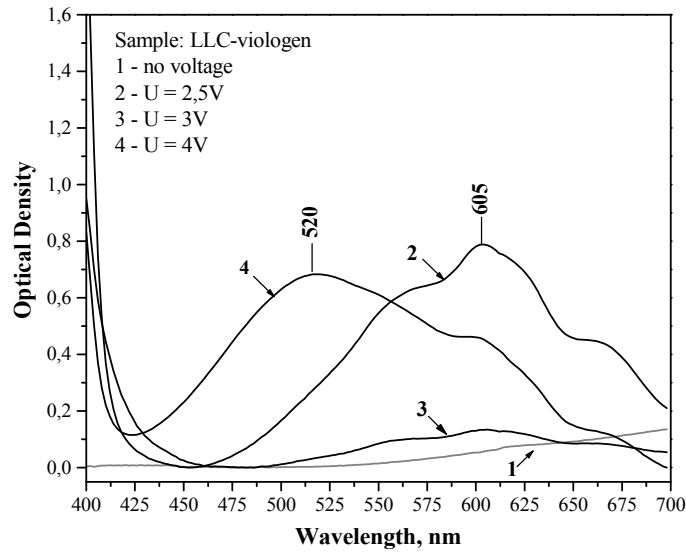


Fig. 1. Absorption spectrum of LLC – viologen composition after applying voltage of different values

Hamiltonian of a physical dimer can be expressed as a sum of Hamiltonians of individual molecules H_1 and H_2 and the energy of an intermolecular interaction V_{12}

$$H = H_1 + H_2 + V_{12}.$$

Neglecting those portions of a wave function, which are associated with oscillations and spin, the electronic wave function of the ground dimer state can be expressed as $\psi_g = \psi_1\psi_2$, where ψ_1 and ψ_2 represent wave functions of the ground state of molecules 1 and 2, respectively. Then, the energy of the ground state of a physical dimer will be equal to:

$$E_g = E_1 + E_2 + \langle \psi_1\psi_2 | V_{12} | \psi_1\psi_2 \rangle,$$

where E_1 and E_2 are the energies of the stationary states of monomers ψ_1 and ψ_2 . The last component represents the Coulomb binding energy W of a pair of monomers, which is negative for dimers and positive for excimers. Excimer refers to a physical dimer in which molecule in the excited electronic state is coupled to the same molecule in the ground state.

When considering excited dimers states corresponding to the lower energy levels let us assume that ψ_1^* and ψ_2^* are equivalent excited electronic states of two equal interacting molecules. If the interaction $V_{12} = 0$, the states $\psi_1^*\psi_2$ and $\psi_1\psi_2^*$ will have the same energy; furthermore, after the excitation of one of the molecules the excitation energy remains at this very molecule. If $V_{12} \neq 0$, two new configurations appear having different energies. The electronic energy is no longer located at one molecule but transfers periodically from one molecule to the other. The difference between the energies of those new configurations depends on the interaction energy and therefore on the mutual orientation of molecules. According to the quantum mechanics the distribution of excitation energy is

characterized by wave functions which are represented by linear combinations of non-excited (initial) states; so that

$$\psi_E = c_1 \psi_1^* \psi_2 + c_2 \psi_1 \psi_2^*.$$

In the case of two identical molecules of monomers excitation are equal ($E_1^* = E_2^*$), and dimers energies $E(\pm)$ are determined by the following formula:

$$E(\pm) = E_1^* + E_2 + W' \pm \beta,$$

here β is the energy of a resonance interaction, which defines energy level splitting between two stationary states

$$\beta = \langle \psi_1^* \psi_2 | V_{12} | \psi_1 \psi_2^* \rangle,$$

and W' represents the Coulomb interaction between distributed charges of the first molecule being in the excited state and the second molecule being in the ground state (or vice versa):

$$W' = \langle \psi_1^* \psi_2 | V_{12} | \psi_1^* \psi_2 \rangle.$$

The corresponding stationary states are:

$$\psi_{E(+)} = 1 / \sqrt{2(\psi_1^* \psi_2 + \psi_1 \psi_2^*)},$$

$$\psi_{E(-)} = 1 / \sqrt{2(\psi_1^* \psi_2 - \psi_1 \psi_2^*)}.$$

If dimer is in one of the stationary states the excitation is distributed between two molecules for all the time. If dimer exists in the non-stationary state, i.e., the excitation is localized at one molecule, provided that there is no energy removal the excitation is transferred from one molecule to another in a wavelike or coherent manner.

Figure 2 illustrates the shift and splitting of energy levels of a dimer relative to the levels of a

monomer. Depending on the values of W and W' and mutual orientation of transition moments of monomers, the shift of spectral bands can occur towards violet or red spectral region (Fig. 3). The allowed dipole transitions are defined by transition

moments, which are equal for the dimeric states $\Psi_{E(+)}$ and $\Psi_{E(-)}$.

$$M_{(\pm)} = 1/\sqrt{2}(M_1 \pm M_2),$$

where M_1 and M_2 are the transition moments of monomers.

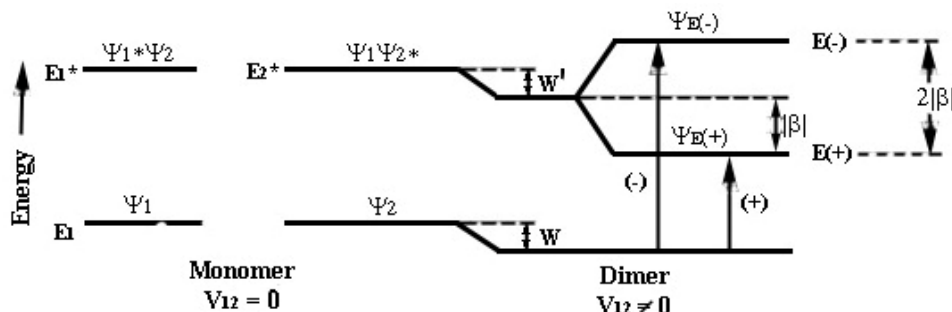


Fig. 2. Exciton zone splitting and energy levels shift for the physical dimer. When $\beta < 0$ the energy state of dimer $\Psi_{E(+)}$ is located lower than the $\Psi_{E(-)}$ state. Two possible optical transitions are shown by arrow lines

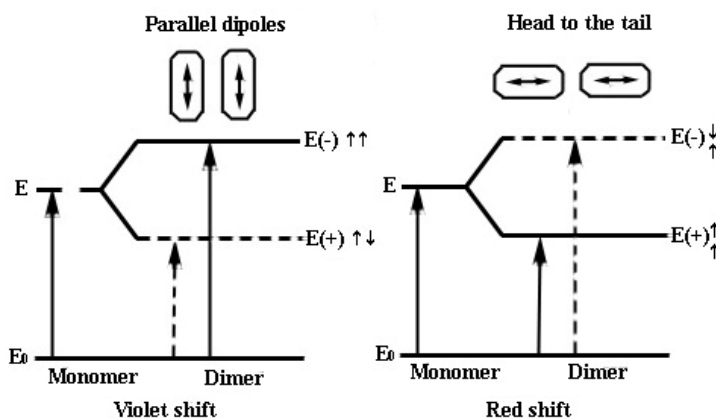


Fig. 3. Exciton splitting for dimers having different geometry. E is the excited state of a monomer; $E(-)$ and $E(+)$ represent dimer levels. The direction of dipole moments of monomers transition is shown by short arrow lines. Dipole-forbidden transitions are shown by dotted lines

In the case of translation-equivalent molecules these moments can be parallel or antiparallel, therefore, for one of the configurations the resulting moment is equal to zero ($M_{(+)} = 0$ or $M_{(-)} = 0$). That is the optical transition is allowed only to the one excited state of a dimer (Fig. 3).

Applying the foregoing theory to the experimental results it is possible to assume the mechanism of dimers formation by viologen molecules. Based on the optical spectra the absorption of a dimeric form of viologen is shifted to the violet region relative to the absorption of radical cations (Fig. 1). That is during the dimers formation molecules are situated parallel to each other as it is shown in Fig. 3. In this case the excitation between antiparallel molecules is forbidden, so the probability of dimer formation by two radical cations is excluded. Therefore, in the case of viologens dimers are formed due to donor-acceptor interaction between reduced viologen molecule with quinoid structure and initial molecule, as described, e.g. in [8].

CONCLUSIONS

1. Experimental data have shown that during the gradual increasing the voltage applied to the LLC-viologen sample between stages of formation of blue-coloured radical cations and red-coloured dimers there is a stage when neither radical cations nor dimers are detected by optical spectrometry.

2. Quantum mechanical theory for physical dimers indicates that according to the observed shift of the absorption band of a dimeric form of viologen towards the violet spectral region relative to the absorption band of radical cations the dimerization process can occur only between two parallel molecules.

3. Together these facts prove that in lyotropic liquid crystal matrix dimerization of viologen molecules occurs due to the interaction between fully reduced and initial viologen molecules.

REFERENCES

- [1] Bordyug, A. B.; Polishchuk, A. P.; Klimusheva, G. V.; Tolochko, A. S.; Mirnaya, T. A., and Yaremchuk, G. G. (2005). "Structure and Intermolecular Interactions in Ionic Liquid Crystals Doped with Electrochromic Viologen". *Russian Journal of Physical Chemistry*. vol. 79, Suppl. 1. pp. 866–870.
- [2] Bordyuh, A.; Garbovskiy, Yu.; Bugaychuk, S.; Klimusheva, G. and Reshetnyak, V. (2009). "Fast nonlinear optical mechanisms in bi-layered cells composed by lyotropic ionic liquid crystals with dye and viologen films". *Mol. Cryst and Liq. Cryst.* vol. 508. pp. 296–308.
- [3] Bordyuh, A. B.; Garbovskiy, Yu. A.; Bugaychuk, S. A.; Klimusheva, G. V.; Mirnaya, T. A.; Yaremchuk, G. G.; Polishchuk, A. P. (2009). "Dynamic grating recording in lyotropic ionic smectics of metal alkanoates doped with electrochromic impurities". *Optical Materials*. vol. 31. pp. 1109–1114.
- [4] Monk, P. M. S. (1998). *The Viologens*. Wiley-VCH, 312 p.
- [5] Grachev, V. N.; Zhdanov, S. I.; Supin G. S. (1978). "The investigation of chemical properties of bis-(0,0-dimethylphosphate)-N,N'-dimethyl-4,4-dipyridilium using methods of classic and alternating current polarography". *Electrochimica*, vol. XIV. pp. 1353–1361. (in Russian).
- [6] Bordyuh, H. B. (2010). "Electrooptical and nonlinear-optical properties of lyotropic ionic liquid crystals with electrochromic admixtures". *Thesis for scientific degree of Candidate of Sciences of Physics and Mathematics* by speciality 01.04.15. Kyiv, Publ., 127 p. (in Ukrainian).
- [7] Kosower, E. M.; Cotter, J. L. (1964). "Stable free radicals. II. The reduction of 1-methyl-4-cyanopyridinium ion to methylviologen cation radical". *J. Amer. Chem. Soc.* vol. 86, no. 24. pp. 5524–5527.
- [8] Monk, P. M. S.; Fairweather, R. D.; Ingram, M. D. and Duffy, J. A. (1993). "Pulsed electrolysis enhancement of electrochromism in viologen systems: influence of comproportionation reactions". *J. Electroanal. Chem.*, vol. 359. pp. 301–306.
- [9] Pope, M.; Swenberg, C. E. (1982). *Electronic Processes in Organic Crystals*. Clarendon Press, 821 p.

Received 08 April 2015.

Bordyuh Hanna. Ph. D. in Physics and Mathematics. Assistant professor. Department of Physics, National Aviation University, Kyiv, Ukraine. Education: National University of Kyiv-Mohyla Academy, Kyiv, Ukraine (2002). Research interests: physics of molecular and liquid crystals. Publications: 16. E-mail: a.bordyuh@gmail.com

Г. Б. Бордюг. Механізм димеризації віологенів у рідкокристалічному середовищі

Представлено аналіз експериментальних даних з оптичних властивостей вміщених у рідкокристалічне середовище віологенів, зумовлених прикладанням зростаючої зовнішньої напруги. Ці дані разом із квантово-механічною теорією дозволили встановити механізм димеризації молекул віологенів, яка призводить до зміни кольору зразка рідкий кристал – віологен. Зокрема, димеризація молекул віологенів у рідкокристалічному середовищі відбувається внаслідок взаємодії між молекулами віологенів, що були повністю відновлені під дією прикладеної напруги, та вихідними молекулами віологенів.

Ключові слова: ліотропні рідкі кристали; віоло гени; оптична спектроскопія; поглинання; квантова механіка.

Бордюг Ганна Борисівна. Кандидат фіз.-мат. наук. Доцент. Кафедра загальної фізики інституту інформаційно-діагностичних систем, НАУ. Київ, Україна. Освіта: Національний університет «Києво-Могилянська Академія», Київ, Україна (2002). Напрямок наукової діяльності: фізика молекулярних та рідких кристалів. Кількість публікацій: 16. E-mail: a.bordyuh@gmail.com

А. Б. Бордюг. Механизм димеризации виологенов в жидкокристаллической среде

Представлен анализ экспериментальных данных по оптическим свойствам внесенных в жидкокристаллическую среду виологенов, обусловленных приложением возрастающего внешнего напряжения. Эти данные вместе с квантово-механической теорией позволили установить механизм димеризации молекул виологенов, которая приводит к изменению цвета образца жидкий кристалл – виологен. В частности, димеризация молекул виологенов в жидкокристаллической среде происходит в результате взаимодействия между молекулами виологенов, которые были полностью восстановлены под действием прикладываемого напряжения, и исходными молекулами виологенов.

Ключевые слова: лиотропные жидки кристаллы; виологены; оптическая спектроскопия; поглощение; квантовая механика.

Бордюг Анна Борисовна. Кандидат физ.-мат. наук. Доцент. Кафедра общей физики института информационно-диагностических систем, НАУ, Киев, Украина. Образование: Национальный университет «Києво-Могилянська Академія», Киев, Украина (2002). Направление научной деятельности: физика молекулярных и жидких кристаллов. Количество публикаций: 16. E-mail: a.bordyuh@gmail.com